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Description

This invention relates to aqueous dispersions and more particularly to aqueous polymer dispersions containing a water-dispersible polyurethane and a vinyl polymer.

5 Aqueous polyurethane dispersions are well known and are used, for example, in the production of coatings and films. Dispersion of the polyurethane in the aqueous system has been achieved by the use either of external surfactants or by including appropriate ionic or nonionic groups in the polyurethane to render it self-dispersible. Thus, for example, U.S. Pat. No. 4066591 describes aqueous dispersions obtained by dispersing an isocyanate-terminated polyurethane prepolymer which contains anionic salt groups in an 10 aqueous medium and then reacting the dispersed prepolymer with an active hydrogen containing chain extender.

It has also been proposed to modify the properties of polyurethane dispersions by including vinyl polymers therein. Several patents, for example U.S. Pats Nos. 3705164, 4198330 and 4318833, describe processes wherein the vinyl polymer is formed *in situ* by polymerising one or more vinyl monomers in the 15 presence of an aqueous dispersion of a polyurethane containing anionic salt groups. In some cases, the polyurethane prepolymer is formed in the presence of, or subsequently diluted with, an organic solvent which serves to reduce the viscosity of the prepolymer and/or facilitate its dispersion in water. The solvent may then be removed from the dispersion by distillation as described in US 3705164, a troublesome procedure, or allowed to remain as described in US 4318833 and possibly adversely affect the final product 20 and/or the environment.

In the process described in EP-A-189945, the polyurethane prepolymer is formed in the presence of vinyl monomer, thereby avoiding the need for conventional solvents. The solution of prepolymer is then dispersed in water, the prepolymer is chain extended and the vinyl monomer is subjected to suspension polymerisation using conventional free radical catalysts. However, this procedure is not entirely satisfactory, 25 the hydrophobicity of some prepolymers and vinyl monomers being such that unstable or gelled dispersions are formed. Additionally, in the production of copolymers, no control over the copolymer composition distribution can be achieved because of the batch nature of the polymerisation process. This is a particular problem when the comonomer reactivity ratios are not well matched.

It has now been found that superior dispersions may be obtained by forming an aqueous dispersion of 30 a solution of a prepolymer containing anionic groups in a selected amount of vinyl monomer (sufficient to provide viscosities suitable for the production of good dispersions) and then polymerising the monomer, either by free radical polymerisation following the addition of further monomer, or by conventional emulsion polymerisation techniques with further addition of monomer during the emulsion polymerisation. Furthermore, it has been found that no additional surfactant is required either at the prepolymer dispersion stage or 35 during polymerisation of the vinyl monomer.

Accordingly, the invention provides a process for the preparation of a surfactant free aqueous polymer dispersion containing an anionic water-dispersible polyurethane and a vinyl polymer in a weight ratio of from 10:90 to 90:10, said process comprising:

- 40 A) forming a solution of an anionic water-dispersible isocyanate-terminated polyurethane in at least one vinyl monomer;
- B) dispersing the solution in an aqueous medium;
- C) chain extending the polyurethane, and subsequently either
- D) adding further vinyl monomer
- 45 and
- E) initiating polymerisation of the vinyl monomer,
- or
- F) initiating polymerisation of the vinyl monomer,
- and
- 50 G) adding further vinyl monomer during polymerisation.

Preferred dispersions made from the process contain the anionic water-dispersible polyurethane and the vinyl polymer in a weight ratio of from 20:80 to 80:20.

55 The anionic water-dispersible isocyanate-terminated polyurethane will be a polyurethane prepolymer having acidic residues providing water-dispersibility. Such prepolymers and methods for their preparation have been fully described in the prior art.

Polyurethane prepolymers having acidic centres include isocyanate-terminated reaction products of:

- i) an organic polyisocyanate;
- ii) a polymeric polyol having a molecular weight of from 500 to 6000;

- iii) an isocyanate-reactive compound having at least one acid group and at least two groups that are more reactive than the acid group towards isocyanates, and, optionally
- iv) a low molecular weight polyol having a molecular weight below 500.

The polyisocyanate used in making the prepolymer may be an aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanate. Examples of suitable polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-xylylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, polymethylene polyphenyl polyisocyanates and 1,5-naphthylene diisocyanate. Mixtures of polyisocyanates can be used and also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Polymeric polyols having molecular weights in the range of 500-6000 which may be used in the preparation of the prepolymer particularly include diols and triols and mixtures thereof but higher functionality polyols may be used, for example as minor components in admixture with diols. The polyols may be members of any of the chemical classes of polymeric polyols used or proposed to be used in polyurethane formulations. In particular, the polyols may be polyesters, polyesteramides, polyethers, polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes. Preferred polyol molecular weights are from 700 to 3000.

Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, furan dimethanol, cyclohexane dimethanol, glycerol, trimethylolpropane or pentaerythritol, or mixtures thereof, with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their methyl esters, phthalic anhydride or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a polyol may also be used. Polyesteramides may be obtained by the inclusion of amino-alcohols such as ethanolamine in polyesterification mixtures.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide or tetrahydrofuran or by the addition of one or more such oxides to polyfunctional initiators, for example water, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol or Bisphenol A. Especially useful polyesters include polyoxypropylene diols and triols, poly (oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to appropriate initiators and polytetramethylene ether glycols obtained by the polymerisation of tetrahydrofuran.

Polythioether polyols which may be used include products obtained by condensing thioglycol either alone or with other glycols, dicarboxylic acids, formaldehyde, aminoalcohols or aminocarboxylic acids.

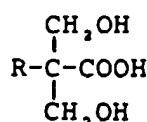
Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Polyacetal polyols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo and copolymers.

Polyols having molecular weights below 500 which may optionally be used in the preparation of the prepolymer particularly include diols and triols and mixtures thereof but higher functionality polyols may be used. Examples of such lower molecular weight polyols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis (hydroxyethyl) terephthalate, cyclohexane dimethanol, furan dimethanol, glycerol and the reaction products, up to molecular weight 499, of such polyols with propylene oxide and/or ethylene oxide.

Isocyanate-reactive compounds containing acid groups which may be used in the preparation of prepolymers having acidic centres include carboxy group containing diols and triols, for example dihydroxy alkanic acids of the formula:



wherein R is hydrogen or alkyl. The preferred carboxy containing diol is 2,2-dimethylolpropionic acid. If desired, the carboxy containing diol or triol may be incorporated into a polyester by reaction with a dicarboxylic acid before being incorporated into the prepolymer. Useful materials include the fumarate polyether glycols described in US 4460738. Other useful acid group containing compounds include amino carboxylic acids, for example lysine, cystine and 3,5-diaminobenzoic acid and sulphonic acids, for example 4,6-diaminobenzene-1,3-disulphonic acid.

The anionic water-dispersible isocyanate-terminated polyurethane prepolymer may be prepared in conventional manner by reacting a stoichiometric excess of the of the organic polyisocyanate with the polymeric polyol having a molecular weight in the range 500 to 6000 and the other required isocyanate-reactive compounds under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until reaction between the isocyanate groups and the hydroxyl groups is substantially complete. The polyisocyanate and the active hydrogen containing components are suitably reacted in such proportions that the ratio of number of isocyanate groups to the number of hydroxyl groups is in the range from about 1.1:1 to about 6:1, preferably within the range of from 1.5:1 to 3:1. If desired, catalysts such as dibutyltin dilaurate and stannous octoate may be used to assist prepolymer formation.

The solution of the water-dispersible polyurethane prepolymer in vinyl monomer may be produced by adding one or more vinyl monomers to the prepolymer or, preferably by forming the prepolymer in the presence of one or more vinyl monomers.

Suitable vinyl monomers in which the prepolymer may be dissolved contain one or more polymerisable ethylenically unsaturated groups. Preferred monomers are liquid under the temperature conditions of prepolymer formation although the possibility of using solid monomers in conjunction with organic solvents is not excluded. It is also preferred to use monomers which do not contain isocyanate or isocyanate-reactive groups.

Thus, suitable monomers include ethylenically unsaturated hydrocarbons, esters and ethers, especially esters of acrylic and methacrylic acids, esters and ethers of vinyl alcohol and styrene. Specific examples include butadiene, isoprene, styrene, substituted styrenes, the lower alkyl (C1-6) esters of acrylic, methacrylic and maleic acids, vinyl acetate, butyrate, acrylate and methacrylate, acrylonitrile, allyl methacrylate, vinyl methyl, propyl and butyl ethers, divinyl ether, divinyl sulphide, vinyl chloride, vinylidene chloride, hexanediol diacrylate, trimethylolpropane triacrylate and the like. Free acids should not be employed since they may destabilise the dispersion.

The prepolymer/vinyl monomer solution may be dispersed in water using techniques well known in the art. Preferably, the solution is added to the water with agitation or, alternatively, water may be stirred into the solution.

The active hydrogen containing chain extender which is reacted with the prepolymer is suitably a polyol, an amino alcohol, ammonia, a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic amine especially a diamine, hydrazine or a substituted hydrazine. Water-soluble chain extenders are preferred, and water itself may be effective.

Examples of suitable chain extenders useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, piperazine, 2-methyl piperazine, phenylene diamine, tolylene diamine, xylylene diamine, tris (2-aminoethyl) amine, 3,3'-dinitrobenzidine, 4,4'-methylenebis (2-chloraniline), 3,3'-dichloro-4,4'-bi-phenyl diamine, 2,6-diaminopyridine, 4,4'-diaminodiphenylmethane, menthane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolyzed products. Also materials such as hydrazine, azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, hydrazides of dicarboxylic acids and sulfonic acids such as adipic acid mono- or dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, tartaric acid dihydrazide, 1,3-phenylene disulfonic acid dihydrazide omega-amino-caproic acid dihydrazide, hydrazides made by reacting lactones with hydrazine such as gamma-hydroxylbutyric hydrazide, bis-semi-carbazide,bis-hydrazide carbonic esters of glycols such as any of the lycols mentioned above.

Where the chain extender is other than water, for example a diamine or hydrazine, it may be added to the aqueous dispersion of prepolymer and vinyl monomer or, alternatively, it may already be present in the aqueous medium when the prepolymer and monomer are dispersed therein.

The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5° to 95°C or more, preferably from about 10° to about 45°C.

The amount of chain extender employed should be approximately equivalent to the free-NCO groups in the prepolymer, the ratio of active hydrogens in the chain extender to NCO groups in the prepolymer preferably being in the range from 0.7 to 2.00:1. Of course when water is employed as the chain extender, these ratios will not be applicable since the water, functioning both as chain extender and dispersing

medium, will be present in a gross excess relative to the free-NCO groups.

The conversion of any acid groups present in the prepolymer to anionic groups may be effected by neutralising the said acidic groups before, after or simultaneously with formation of the aqueous dispersion. Suitable neutralising agents include tertiary amines such as triethylamine.

5 Polymerisation of the vinyl monomer or monomers may be effected by one of two methods.

In the first method, additional monomer (the same or different vinyl monomer or monomer mixture) is added and may swell the polyurethane. The monomer may then be polymerised using a conventional free radical initiator system. The proportion of monomer used as solvent for the prepolymer is suitably from 1.5 to 95%, preferably from 2.5 to 80% and more preferably from 7 to 50% by weight of the total monomers.

10 In the second method, polymerisation of the vinyl monomer diluent and feeding of the same or a different vinyl monomer or monomer mixture is allowed to continue until complete. The proportion of monomer used as solvent for the prepolymer may be as indicated for the first method.

In either method of polymerisation, the vinyl monomers which may be added and polymerised include those mentioned above. Functional monomers such as hydroxyalkyl acrylates and methacrylates may also 15 be incorporated at this stage since the free isocyanate groups of the prepolymer will have reacted with the chain extender.

Suitable free radical initiators include mixtures partitioning between the aqueous and organic phases, for example a combination of t-butyl hydroperoxide, isoascorbic acid and Fe.EDTA.

20 The aqueous polymer dispersions produced by the method of the invention are stable for long periods of time despite the absence of emulsifiers. If desired, minor amounts of solvents may be included in the dispersions.

The dispersions obtained by the method of the invention may be employed as coating compositions and may be applied to any substrate including wood, metals, glass, cloth, leather, paper, plastics, foam and the like, by a conventional method including brushing, dipping, flow coating, spraying and the like. Films 25 obtained from the coating compositions may be used as adhesives in the production of composite articles.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

Example 1

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A prepolymer solution was prepared from the following ingredients:

	Parts
35	Isophorone diisocyanate
	33.9
	Dimethylolpropionic acid
	6.0
	Polycarbonate diol
	58.9
	Trimethylolpropane
	0.6
	Cyclohexane dimethanol
	0.6
40	Methyl methacrylate
	42.8

The prepolymer solution was then neutralised with triethylamine, dispersed in water and extended with ethylene diamine using no surfactant.

45 A monomer mixture containing 97.2 parts of methyl methacrylate and 93 parts of butyl acrylate was added to the polyurethane dispersion and swollen in.

Polymerisation was effected using t-butyl hydroperoxide and isoascorbic acid.

The resulting polymer dispersion was translucent, had a low viscosity and contained a small amount of sediment.

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Example 2

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A polyurethane dispersion was prepared as described in Example 1. Polymerisation was initiated using t-butylhydroperoxide and isoascorbic acid. During polymerisation, a monomer mixture containing 97.2 parts of methyl methacrylate and 93 parts of butyl acrylate was fed in.

The resulting polymer dispersion was again translucent, of low viscosity and had a low sediment content.

Comparative Example C1

A prepolymer solution was prepared from the following ingredients:

	Parts
5	
	Isophorone diisocyanate 33.9
	Dimethylolpropionic acid 6.0
	Polycarbonate diol 58.9
	Trimethylolpropane 0.6
	Cyclohexane dimethanol 0.6
10	
	Methyl methacrylate 140
	Butyl acrylate 93

The prepolymer solution was then neutralised with triethylamine, dispersed in water to 35% solids (including monomer) and extended with ethylene diamine.

15 The product was a white hazy dispersion with coarse particle size and heavy sediment. Phase separation occurred after 3 days.

Initiation with t-butyl hydroperoxide and isoascorbic acid after 1 day resulted in coagulation at the start of the polymerisation.

20 Example 3

A. Polyurethane preparation

25 The urethane prepolymer was prepared in a fourneck round bottom flask, equipped with a thermometer, mechanical stirrer, condenser, dry air or nitrogen blanket and heating mantle, by using the following formulation:

	Parts
30	
	Isophorone diisocyanate 525.00
	Terathane-1000 (OH number - 114.3mg KOH/g) 635.33
	Dimethylolpropionic acid 81.25
	1,4-Cyclohexane dimethanol 8.43
35	
	Catalyst: dibutyltinlaurate 0.15
	Butyl acrylate 313.85
	Inhibitor:Topanol O 0.63

40 Half of the dibutyltinlaurate was added before heating the mixture of diisocyanate and polyols and the other part after 1 hour at reaction temperature. 139.56 parts of the butyl acrylate were added before reaction, the remaining parts were used for diluting the prepolymer after the reaction. The inhibitor was equally divided over the butyl acrylate. Total reaction time took 2 hours, the reaction temperature was maintained at 90-95 °C. The residual NCO content was 5.59% (theoretical 5.64%).

45 The prepolymer was neutralized by mixing in 60.13 parts triethylamine at 50-60 °C for half an hour. The neutralized prepolymer was dispersed in 3071.69 parts of demineralized water during 60 minutes. After dispersion, 44.17 parts hydrazine monohydrate were added to chain extend the NCO terminated prepolymer. The resulting polyurethane dispersion had a pH of 7.8, a Brookfield viscosity at 25 °C of 37mPas and solids content of 27.3%.

(Terathane 1000 is a polytetramethylene glycol)

50 B. Urethane vinyl polymer preparation

The radical polymerisation for producing the polymer dispersion having a urethane-acrylic polymer ratio of 40/60 was carried out using the following process:

55 In similar equipment under a nitrogen blanket were charged 1136.19 parts of the dispersion 508.66 parts demineralized water and 2.25 parts of tert. butyl hydroperoxide. To this dispersion were added 10% of the monomer feed listed below and 9 parts of a 2% i-ascorbic acid solution in water. (neutralized with ammonia to pH 7-9). After heating to 75 °C, the remaining monomer feed was added over 60 minutes. The

temperature was maintained at $75 \pm 2^\circ\text{C}$ for 75 minutes. After the i-ascorbic acid feed was completed, the reaction medium was brought to $80-82^\circ\text{C}$ for half an hour post-reaction before cooling.

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Monomer feed:	
	Parts
Methyl methacrylate	301.95
Butyl Methacrylate	58.05
Butyl acrylate	15.00
Dimethyl ethanol amine	0.45

10

The obtained polyurethane-acrylic monomer showed the following specification; free monomer content of 0.02%, 0.14% sediment, pH of 8.0, a Brookfield viscosity at 25°C of 160 mPas and contained 37.5% solids. The minimum film forming temperature was lower than 20°C . The end product had a blue white, nearly translucent appearance, the measured absorbance by spectrometry at 650nm using a path length of 1mm was 5.1. Some increase of viscosity was noticed after 4 weeks storage test at 50°C . The film cast on a glass plate with film thickness of 30 μm dry showed a könig hardness of 136 sec. Ethanol and methyl ethyl ketone double rubs were 43x and 155x respectively.

15

Example 4

A. Polyurethane preparation

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Preparation of a polyurethane dispersion was by a procedure similar to that of Example 3, the prepolymer being based on polycarbonate diol and a triol and methyl methacrylate being used as reactive diluent.

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Prepolymer components:	
	Parts
Isophorone diisocyanate	536.32
Permanol KM-10-122 (OH = 55.49mg KOH/g)	930.68
Dimethylolpropionic acid	94.80
Trimethylolpropane	9.48
1,4-cyclohexane dimethanol	8.89
dibutyltinlaurate catalyst	0.19
Methyl methacrylate	678.21
Topanol O inhibitor	1.36

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The prepolymer reaction took 3 hours. The 90% solution in methyl methacrylate was further diluted till 80% and 70% after 1 and 2 hours reaction time.

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Components for preparing the polyurethane dispersion.	
	Parts
Prepolymer	685.71
Triethylamine	21.28
Demineralized water	1260.02
Ethylene diamine	20.73

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The low viscous translucent urethane dispersion contained 25.3% solids, <0.02% sediment was found.

B Urethane vinyl polymer preparation

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Components:	
	Parts
Polyurethane dispersion	372.70
Deminerlized water	265.87
Tert. butylhydroperoxide	1.31
iso-ascorbic acid solution 1% in water	63.80
Methyl methacrylate	87.43
Butyl acrylate	84.00
Dimethyl ethanolamine	0.21
The urethane vinyl polymer ratio was 30/70.	

Specifications:	
Solids	34.3%
pH	7.7
viscosity at 25 °C	10 mPas
sediment	<0.02%
appearance	blue-white
Absorbance (at 650nm)	31
minimum film forming temperature	<15 °C

Film properties:	
König hardness	78 sec
Ethanol double rub	18x
MEK double rub	48x

35 Example 5

A polyurethane vinyl polymer was prepared using a urethane dispersion and other components in the recipe for the radical polymerization as described in Example 4.

However, the radical polymerization procedure was as follows:

40 First addition of the monomer blend to the diluted polyurethane dispersion, followed by addition of tert. butyl hydroperoxide and 10% of the iso-ascorbic acid solution.

Further feeding of the iso-ascorbic acid solution at 40 °C resulted in an exothermic reaction, causing a peak temperature at 79 °C. After 30 minutes feeding time and 30 minutes post-reaction at 80-82 °C, a free monomer content was found at 0.02%

Other specifications are	
Solids	34.3%
pH	7.9
Viscosity at 25 °C	10 mPas
Sediment	<0.02%
Appearance	blue-white
Absorbance	24
minimum film forming temperature	23 °C
The urethane vinyl ratio was 30/70.	

Comparative Example C2

The polyurethane prepolymer, described in Example 4, was diluted with methyl methacrylate and butyl acrylate so that the final urethane vinyl polymer ratio should become 30/70. the recipe for dispersing this prepolymer was as follows:

5

	Parts:
Polyurethane prepolymer	285.71
Methyl methacrylate	194.29
Butyl acrylate	186.67
Triethylamine	8.87
Demineralised water	1245.27
Ethylenediamine	8.64

10

Neutralising, dispersing and chain extending the prepolymer-monomer blend resulted in a hazy white mixture with a coarse particle size and much sediment. Solids including the monomers was 35%. Phase separation occurred after 3 days.

This product was subjected to a radical polymerization after 1 day. First adding the tert. butyl-hydroperoxide and feeding the iso-ascorbic acid at 40 °C did not result in an exothermic reaction; heating to 60 °C also did not result in an exothermic reaction. Finally, the mixture gelled after 75 minutes reaction time.

Example 6

A. Polyurethane preparation

The procedure was identical to Example 3. However, the urethane polymer, was modified with a triol and a tetra functional amine. The prepolymer was prepared in presence of 134.63 parts of butyl acrylate. The residual butyl acrylate and acrylonitrile were used for dilution after completing the prepolymer reaction, but before the dispersion step. Ethylene diamine and triethylene tetramine were used as extension agents.

35

Prepolymer components:	
	parts:
Isophorone diisocyanate	512.69
Terathane-1000 (OH = 114.3 mg KOH/g)	595.80
Dimethylol propionic acid	78.00
Trimethylol propane	13.51
dibutyltinlaurate catalyst	0.14
Butyl acrylate	150.74
Acrylonitrile	150.74
Inhibitor Topanol O	0.60

The prepolymer contained 5.16% NCO (theoretical 5.73%).

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Components for preparing the polyurethane dispersion.

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	parts:
Prepolymer	1502.22
Triethylamine	57.73
Demineralized water	3416.47
Ethylene diamine	51.39
Tri ethylene tetra amine	6.42

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The polyurethane dispersion showed a translucent appearance. The solids content was 25%.

B. Urethane vinyl polymer preparation

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According to the procedure described in Example 3, the following components were used for the polymerization:

		parts:
5	polyurethane dispersion	670.24
	Demineralized water	203.36
10	Tert. butyl hydroperoxide	1.50
	Iso-ascorbic acid solution, 1% in water	72.75
	Butyl acrylate	52.00
	Methyl methacrylate	84.00
	Acrylonitrile	52.00
	Allyl methacrylate	12.00
15	Dimethyl ethanol amine	0.24

Since 0.60% free monomer was still present, a post-reaction with ammonium persulphate was necessary.

Therefore, 4.67 g of a 10% ammonium persulphate solution (neutralized with ammonia to pH 8) was added and the reaction mixture was heated to 90-92 °C and held at this temperature for half an hour before cooling. The free monomer content was then 0.06%.

The polyurethane-vinyl polymer ratio was 40/60.

The specification of the resulting dispersion was as follows:

25	solids	35.2%
	pH	8.0
	viscosity at 25 °C	600 mPas
30	sediment	0.30%
	minimum film forming temperature	16 °C
	appearance	blue white
	absorbance (at 650 nm)	31

The storage stability at 50 °C was insufficient, in the third week the polymer gelled. However, at ambient temperature, the dispersion was stable for more than one year.

Film properties:	
König hardness	144 sec
Ethanol double rub	15x
MEK double rub	20x

Example 7

45 This Example describes the preparation of a urethane-vinyl polymer with the same polyurethane dispersion, same components in the same ratios and a comparable radical polymerization as in Example 6, but a sequential monomer feed was used for introducing acrylonitrile in the first and 90% of the allyl methacrylate in the second feed.

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55

Recipe for the radical polymerization:	
	Parts:
5	Polyurethane dispersion 670.24
	Demineralized water 203.36
	Tert butyl hydroperoxide 1.50
	Iso ascorbic acid solution, 1% in water 72.75
10	First monomer feed:
	Butyl acrylate 30.40
	Methyl methacrylate 58.80
	Acrylonitrile 52.00
	Allyl methacrylate 1.20
	Dimethyl ethanol amine 0.17
15	Second monomer feed:
	Butyl acrylate 21.60
	Methyl methacrylate 25.20
	Allyl methacrylate 10.80
	Dimethyl ethanol amine 0.07
	The urethane-vinyl ratio was 40/60.
	The ratio first/second monomer feed was 70/30.

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Specification:	
30	solids 35.1%
	pH 8.5
	viscosity at 25 °C 111 mPas
	sediment 0.08%
	free monomer 0.02%
	minimum film forming temperature 16 °C
35	appearance blue white
	absorbance (at 650 nm) 25
	storage stability at 50 °C, for 4 weeks OK

40

Film properties:	
König hardness	135 sec
Ethanol double rub	20x
MEK double rub	31x

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Example 8

50 Polyurethane-vinyl polymer based on the polyurethane dispersion as mentioned in Example 3, the acrylic part being modified with styrene. The urethane-vinyl polymer ratio was 50/50.

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Recipe for the radical polymerization:	
	parts:
Polyurethane dispersion (30.0% solids)	1340.20
Demineralized water	245.75
Tert butyl hydroperoxide	2.46
Iso-ascorbic acid solution, 1% in water	116.78
Styrene	141.51
Methyl methacrylate	117.92
Acrylonitrile	35.38

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Specification:	
solids	35.4%
pH	8.0
viscosity at 25 °C	19 mPas
sediment	0.02%
free monomer	0.40%
minimum film forming temperature	< 15 °C
absorbance (at 650 nm)	19
appearance	blue white

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Film properties:	
König hardness	101 sec
Ethanol double rub	10x
MEK double rub	10X

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Polyurethane vinyl polymer based on the polyurethane dispersion as described in Example 3, the acrylic part modified with styrene as in Example 8, but with a polyurethane-vinyl polymer ratio of 20/80.

Recipe for the radical polymerization:	
	Parts:
Polyurethane dispersion (30.0% solids)	496.72
Demineralized water	778.30
Tert butylhydroperoxide	3.64
Iso-ascorbic acid solution, 1% in water	175.00
Styrene	209.79
Methyl methacrylate	174.83
Acrylonitrile	52.45
Butyl acrylate	109.24

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Specification:	
5	Solids 35.7%
	pH 7.7
	Viscosity at 25 °C 16 mPas
10	Sediment 0.03%
	Free monomer 0.25%
	Minimum film forming temperature 43 °C
	Absorbance 31
	Appearance blue-white

Film properties:	
15	König hardness 180 sec
	Ethanol double rub 30x
	MEK double rub 30x

20 Example 10

A. Polyurethane preparation

25 A polyesterdiol based polyurethane was prepared following the procedure of Example 1. The prepolymer was diluted with the butyl acrylate-Topanol O solution, but not until the prepolymer preparation was finished.

Prepolymer components		
	Parts:	
30	Isophorone diisocyanate 1561.44	
	Ruco S-1063-120 polyester (OH = 116.7 mg KOH/g) 1542.33	
35	Dimethylol propionic acid 218.24	
	1,4-Cyclohexane dimethanol 38.68	
	dibutyltinlaurate catalyst 0.40	
	Butyl acrylate 839.77	
40	Topanol O inhibitor 1.68	
	The prepolymer contained 6.51% NCO (7.04% NCO theoretical).	

Recipe for preparing the polyurethane dispersion:	
45	Prepolymer 3200.00
	Triethylamine 123.00
	Demineralized water 5523.33
	Ethylene diamine 134.14

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Specification of polyurethane dispersion:	
Solids	26.0%
pH	7.5
Viscosity at 25 °C	28 mPas
Sediment	0.08%
Appearance	blue-white

10 B. Urethane-vinyl polymer preparation

Radical polymerization was according to the procedure of Example 3. However, the iso-ascorbic acid reducing agent was replaced by sodium sulphoxylate formaldehyde.

15 The following recipe was used:

20

		Parts:
Polyurethane dispersion		1067.41
Demineralized water		455.06
Tert butylhydroperoxide		2.62
Sodium sulphoxylate formaldehyde, 1% in water		126.00
Methyl methacrylate		280.94
Butyl methacrylate		54.01
Butyl acrylate		13.96

25

The urethane-vinyl polymer ratio was 40/60.

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Specification:	
Solids	34.6%
pH	8.1
Viscosity at 25 °C	9 mPas
Sediment	0.10%
Free monomer	0.12%
Minimum film forming temperature	39 °C
Absorbance (at 650 nm)	56
Appearance	hazy, white

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Film properties:	
König hardness	163 sec
Ethanol double rub	30x
MEK double rub	120x

50 Example 11

A. Polyurethane preparation

55 A polycaprolactonediol and 4,4'-methylene bis (cyclohexyl) diisocyanate based polyurethane was prepared as described in Example 3. Butyl acrylate and the catalyst were added before starting the prepolymer preparation. The reaction temperature was held at 80-85 °C for 2 hours.

Prepolymer components	
	Parts:
5	4,4'-methylene bis (cyclohexyl) diisocyanate Polycaprolactonediol (OH = 92.7 mg KOH/g)
	Dimethylol propionic acid
	dibutyltinlaurate catalyst
10	Butyl acrylate
	Topanol O inhibitor
	The prepolymer contained 4.20% NCO (theoretical 4.42%).

Recipe for preparing the urethane dispersion:	
	Parts:
15	Prepolymer
20	Triethylamine
	Demineralized water
	Hydrazine monohydrate

Specification of polyurethane dispersion:	
25	Solids
	pH
30	Sediment
	Viscosity at 25 ° C
	Appearance

B. Urethane-vinyl polymer preparation

35 Radical polymerization according to Example 3.

Recipe:	
	Parts:
40	Polyurethane dispersion
	Demineralized water
45	Tert butylhydroperoxide
	Iso-ascorbic acid, 1% solution in water
	Methyl methacrylate
	Butyl methacrylate
	The urethane-vinyl polymer was 50/50.

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Specification:	
5	Solids 33.5%
	pH 8.0
	Viscosity at 25°C 17 mPas
	Sediment < 0.02%
	Free monomer 0.11%
	Minimum film forming temperature 31°C
10	Absorbance 7.7
	Appearance blue-white

Film properties:	
15	König hardness 150 sec
	Ethanol double rubs 140x
	MEK double rubs > 200x

20 Example 12

A. Polyurethane preparation

25 Polyurethane based on toluene diisocyanate (80/20 ratio for the 2.4 and 2.6 isomers) and diphenylmethane diisocyanate (75/25 ratio for the 4.4' and 2.4' isomers).

Recipe for prepolymer preparation:	
	Parts:
30	Toluene diisocyanate 246.00
	Diphenylmethane diisocyanate 246.00
	Terathane-1000 polyetherdiol (OH = 114.3 mg KOH/g) 579.24
35	1,4-Cyclohexane dimethanol 8.76
	Dimethylol propionic acid 120.00
	Butyl acrylate 133.33
	Methyl methacrylate 266.67
	Styrene 400.00
40	Topanol O inhibitor 1.60

45 The urethane prepolymer was prepared by first feeding the polyetherdiol and 1,4-cyclohexyl dimethanol blend to the diisocyanate solution in 1 hour and maintaining the reaction temperature at 50-55°C. The procedure was continued by the addition of dimethylol propionic acid in 1 hour while keeping the temperature at 55-60°C. The reaction mixture was held at 55-60°C for another 6 hours and 2 hours at 65-70°C. In the meantime, the mixture was diluted with butyl acrylate, methyl methacrylate and styrene after 3, 9 and 10 hours reaction time. The NCO content was then 3.73%. (Theoretical 3.25%).

50 The urethane dispersion was prepared by the addition of 400.00 parts prepolymer in 1 hour to an aqueous phase which contain 26.05 parts triethyl amine, 1.04 parts hydrazine and 841.18 parts water. The residual 0.35 parts hydrazine were simultaneously fed, also in 1 hour at ambient temperature.

Specification of polyurethane dispersion:	
Solids	24.1%
pH	8.2
Viscosity at 25 °C	900 mPas
Sediment	0.04%
Absorbance	19
Appearance	blue-white

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B. Urethane-vinyl polymer preparation

Radical polymerization following the procedure described in Example 3.

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Recipe:	
	Parts:
Polyurethane dispersion	851.75
Demineralized water	309.62
Tert butyl hydroperoxide	1.25
Iso ascorbic acid, 1% solution in water	60.00
Styrene	88.60
Methyl methacrylate	15.56
Acrylonitrile	18.00
Butyl acrylate	11.10

The urethane-vinyl polymer ratio was 50/50.

Specification:	
Solids	30.1%
pH	8.1
Viscosity at 25 °C	29 mPas
Sediment	0.40%
Free monomer	0.20%
Absorbance	143
Appearance	slightly hazy, white-yellow

45

Film properties:	
König hardness	136 sec
Ethanol double rub	> 200x
MEK double rub	80x

50 Example 13

A. Polyurethane preparation

The urethane polymer was prepared by a procedure similar to that of Example 3, but was modified with 55 ethylene diamine and a tetra functional amine. The 90% prepolymer in butyl acrylate was further diluted to 80% after the prepolymer preparation:

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Prepolymer components:	
	Parts:
5	Isophorone diisocyanate 672.00
	Terathane-1000 polyether (OH = 114.3 mg KOH/g) 813.22
	Dimethylol propionic acid 104.00
	1,4-Cyclohexane dimethanol 10.78
	dibutyltinlaurate catalyst 0.20
10	Butyl acrylate 400.00
	Topanol O inhibitor 0.80
	The prepolymer contained 5.42% NCO. (Theoretical 5.64%).

Recipe for preparing the polyurethane dispersion:	
	Parts:
20	Prepolymer 600.00
	Triethylamine 23.08
	Demineralized water 1212.89
	Ethylene diamine 19.13
	Triethylene tetramine 2.39

Specification of polyurethane dispersion:	
30	Solids 27.5%
	pH 7.7
	Viscosity at 25 °C 27
	Sediment >0.02%
	Absorbance (at 650 nm) 2.1
	Appearance translucent

B. Urethane-vinyl polymer preparation	
Radical polymerization based on azo-bis (isobutyronitrile) initiator. Diallyl phthalate was incorporated as difunctional component.	
The procedure was as follows:	
40	The monomer blend including the initiator were fed to the diluted polyurethane dispersion for 1 hour, keeping the reaction temperature at 80 ± 2 °C. After half an hour postreaction at 90 ± 2 °C, a free monomer content was found of 0.02%.
45	Recipe for radical polymerization:
50	Parts:
	Urethane dispersion 483.73
	Demineralized water 162.24
	Azo-bis (isobutyronitrile) 0.75
	Butyl acrylate 2.24
	Butyl methacrylate 12.50
	Methyl methacrylate 78.39
55	Diallyl phthalate 0.63
	The urethane-vinyl polymer ratio was 50/50.

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Specification:	
Solids	32.3%
pH	8.6
Viscosity at 25 °C	82
Sediment	1.0%
Free monomer	0.02%
Absorbance (at 650 nm)	18
Appearance	blue-white

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Example 14

15 A. Polyurethane preparation

Urethane polymer based on Terathane-2000 polyether diol and 4,4'-methylene bis (cyclohexyl) diisocyanate, prepared as described in Example 3. The catalyst was totally added before and methyl methacrylate was added after finishing the prepolymer preparation.

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Prepolymer components:	
	Parts:
4,4'-Methylene bis (cyclohexyl) diisocyanate	1266.15
Terathane 2000 polyetherdiol (OH = 56.7 mg KOH/g)	1693.85
Dimethyl propionic acid	240.00
dibutyltinlaurate catalyst	1.23
Methyl methacrylate	799.98
Topanol O inhibitor	1.60

30 The prepolymer contained 4.36% NCO (theoretical 4.47%).

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Recipe for preparing the polyurethane dispersion:	
	Parts:
Prepolymer	3100.00
Triethylamine	138.97
Demineralized water	6403.72
Hydrazine monohydrate	71.69

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Specification of the polyurethane dispersion:	
Solids	26.1
pH	8.3
Viscosity at 25 °C	19mPas
Sediment	0.02%
Absorbance (at 650 nm)	0.1
Appearance	clear, colourless

50

55

B. Urethane-vinyl polymer preparation

The radical polymerization, with a urethane-vinyl polymer ratio of 70/30 was carried out as follows:

A dimethyl ethanol amine (DMEA) neutralized mixture of 0.34 parts tert butyl hydroperoxide and 22.90 parts demineralized water (pH = 8.0) was blended with 500 parts of above described urethane dispersion in

the reactor. 0.17 parts isoascorbic acid dissolved in 17.00 parts demineralized water was neutralized with DMEA till pH = 8.0. 10% of this mixture was added to the reactor phase. The reaction mixture was heated till 85°C. When the reaction mixture reached 75°C the monomer feed was started. Total feed-time for the monomer mixture was 15 minutes. At the same time with the monomer feed the remaining isoascorbic acid solution was fed in. This feed lasted for 30 minutes. After completion of this, the mixture was kept at 85°C for another 30 minutes after which the reactor was stripped at 85°C for 30 minutes.

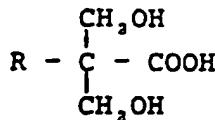
The specification of the 70/30 urethane/acrylate dispersion was as follows:

10	Solids	33.0
	pH	7.7
	Viscosity at 25°C	30
	Sediment	< 0.02%
15	Minimum film forming temperature	< 15
	Appearance	blue-white

[The words Terathane, Permanol, Ruco and Topanol used herein are known to be registered trade marks.]

20 Claims

1. A process for the preparation of a surfactant-free aqueous polymer dispersion containing an anionic water-dispersible polyurethane and a vinyl polymer in a weight ratio of from 10:90 to 90:10, said process comprising:
 - (A) forming a solution of an anionic water-dispersible isocyanate-terminated polyurethane in at least one vinyl monomer;
 - (B) dispersing the solution in an aqueous medium;
 - (C) chain extending the polyurethane, and subsequently either
 - (D) adding further vinyl monomer, and
 - (E) initiating polymerisation of the vinyl monomer, or
 - (F) initiating polymerisation of the vinyl monomer, and
 - (G) adding further vinyl monomer during polymerisation.
2. A process according to claim 1, wherein the dispersion formed contains the water-dispersible polyurethane and the vinyl polymer in a weight ratio of from 20:80 to 80:20.
3. A process according to claim 1 or claim 2 wherein the anionic water-dispersible isocyanate-terminated polyurethane is a reaction product of:
 - (i) an organic polyisocyanate;
 - (ii) a polymeric polyol having a molecular weight of from 500 to 6000;
 - (iii) an isocyanate-reactive compound having at least one acid group and at least two groups that are more reactive than the acid group towards isocyanates, and, optionally
 - (iv) a low molecular weight polyol having a molecular weight below 500.
4. A process according to any preceding claim wherein the isocyanate-reactive compound having at least one acid group is a carboxy group containing diol or triol
5. A process according to claim 4 wherein the carboxy group containing diol or triol is a dihydroxy alkanoic acid of the formula:



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wherein R is hydrogen or alkyl.

6. A process according to claim 5 wherein R is methyl.
7. A process according to any preceding claim wherein the vinyl monomer is selected from methyl methacrylate, butyl acrylate, butyl methacrylate, acrylonitrile, allyl methacrylate, styrene and mixtures of
5 two or more of said monomers.
8. A process according to any preceding claim wherein the proportion of monomer used as solvent for the isocyanate-terminated polyurethane in step A is from 1.5 to 95% by weight of the total monomers.
10. 9. A process according to claim 8 wherein the proportion of monomer used as solvent is from 2.5 to 80% by weight of the total monomers.
15. 10. A process according to claim 9 wherein the proportion of monomer used as solvent is from 7 to 50% by weight of the total monomers.
11. A coating or film derived from a dispersion prepared by the process as claimed in any of claims 1 to
10.
12. A composite article which includes a film as claimed in claim 11 as an adhesive layer.

20 **Patentansprüche**

1. Verfahren zur Herstellung einer tensidfreien wässrigen Polymerdispersion, welche ein anionisches wasserdispergierbares Polyurethan und ein Vinylpolymer in einem Gewichtsverhältnis von 10 : 90 bis
25 90 : 10 enthält, bei welchem Verfahrena) eine Lösung eines anionischen, wasserdispergierbaren, isocyanatabgeschlossenen Polyurethans in mindestens einem Vinylmonomer hergestellt wird,
b) die Lösung in einem wässrigen Medium dispergiert wird,
c) das Polyurethan kettenverlängert wird und anschließend entweder
30 d) weiteres Vinylmonomer zugegeben wird und
e) die Polymerisation des Vinylmonomers initiiert wird, oder
f) die Polymerisation des Vinylmonomers initiiert wird und
g) weiteres Vinylmonomer während der Polymerisation zugegeben wird.
35. 2. Verfahren nach Anspruch 1, bei welchem die hergestellte Dispersion das wasserdispergierbare Polyurethan und das Vinylpolymer in einem Gewichtsverhältnis von 20 : 80 bis 80 : 20 enthält.
3. Verfahren nach Anspruch 1 oder 2, bei welchem das anionische, wasserdispergierbare, isocyanatabgeschlossene Polyurethan ein Reaktionsprodukt ist aus
40 i) einem organischen Polyisocyanat,
ii) einem polymeren Polyol mit einem Molekulargewicht von 500 bis 6000,
iii) einer isocyanatreaktiven Verbindung mit mindestens einer Säuregruppe und mindestens zwei Gruppen, die gegenüber Isocyanaten reaktiver sind als die Säuregruppe, und gegebenenfalls
iv) einem niedermolekularen Polyol mit einem Molekulargewicht unter 500.
45. 4. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die isocyanatreaktive Verbindung mit mindestens einer Säuregruppe eine Carboxygruppe enthaltendes Diol oder Triol ist.
50. 5. Verfahren nach Anspruch 4, bei welchem das eine Carboxygruppe enthaltende Diol oder Triol eine Dihydroxyalkansäure der Formel



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ist, worin R für Wasserstoff oder Alkyl steht.

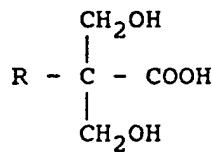
6. Verfahren nach Anspruch 5, bei welchem R für Methyl steht.
- 15 7. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem das Vinylmonomer ausgewählt ist aus Methylmethacrylat, Butylacrylat, Butylmethacrylat, Acrylonitril, Allylmethacrylat, Styrol und Gemischen aus zwei oder mehr dieser Monomere.
- 20 8. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem der Anteil des als Lösungsmittel für das isocyanatabgeschlossene Polyurethan in der Stufe A verwendete Monomer 1,5 bis 95 Gew.% der gesamten Monomere ausmacht.
- 25 9. Verfahren nach Anspruch 8, bei welchem der Anteil des als Lösungsmittel verwendeten Monomers 2,5 bis 80 Gew.% der gesamten Monomere ausmacht.
- 30 10. Verfahren nach Anspruch 9, bei welchem der Anteil des als Lösungsmittel verwendeten Monomers 7 bis 50 Gew.% der gesamten Monomere ausmacht.
11. Belag oder Film, welcher sich von einer durch das Verfahren nach einem der Ansprüche 1 bis 10 hergestellten Dispersion ableitet.
12. Verbundgegenstand, welcher einen Film nach Anspruch 11 als Klebstoffschicht enthält.

Revendications

- 35 1. Procédé de préparation d'une dispersion aqueuse de polymères, dépourvue de surfactant, contenant un polyuréthane anionique dispersable dans l'eau et un polymère vinylique en un rapport pondéral de 10:90 à 90:10, ledit procédé consistant :
 - (A) à former une solution d'un polyuréthane anionique à terminaison isocyanate dispersable dans l'eau dans au moins un monomère vinylique ;
 - (B) à disperser la solution dans un milieu aqueux ;
 - (C) à allonger la chaîne du polyuréthane, puis soit
 - (D) à ajouter une quantité supplémentaire de monomère vinylique, et
 - (E) à déclencher la polymérisation du monomère vinylique, soit
 - (F) à déclencher la polymérisation du monomère vinylique, et
 - (G) à ajouter une quantité supplémentaire de monomère vinylique au cours de la polymérisation.
- 40 2. Procédé suivant la revendication 1, dans lequel la dispersion formée contient le polyuréthane dispersable dans l'eau et le polymère vinylique en un rapport pondéral de 20:80 à 80:20.
- 45 3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel le polyuréthane anionique à terminaison isocyanate dispersable dans l'eau est un produit de réaction :
 - (i) d'un polyisocyanate organique ;
 - (ii) d'un polyol polymérique ayant un poids moléculaire de 500 à 6000 ;
 - (iii) d'un composé réactif avec les isocyanates, comprenant au moins un groupe acide et au moins deux groupes qui sont plus réactifs avec ces isocyanates que le groupe acide et, facultativement
 - (iv) d'un polyol de bas poids moléculaire, ayant un poids moléculaire inférieur à 500.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le composé réactif avec les isocyanates, possédant au moins un groupe acide, est un diol ou triol contenant un groupe carboxy.

5. Procédé suivant la revendication 4, dans lequel le diol ou triol contenant un groupe carboxy est un acide dihydroxyalcanoïque de formule :



dans laquelle R représente l'hydrogène ou un groupe alkyle.

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6. Procédé suivant la revendication 5, dans lequel R représente un groupe méthyle.

7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le monomère vinylique est choisi entre le méthacrylate de méthyle, l'acrylate de butyle, le méthacrylate de butyle; l'acrylonitrile, le méthacrylate d'allyle, le styrène et des mélanges de deux ou plus de deux de ces monomères.

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8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la proportion de monomère utilisé comme solvant pour le polyuréthane à terminaison isocyanate dans l'étape A va de 1,5 à 95% en poids des monomères totaux.

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9. Procédé suivant la revendication 8, dans lequel la proportion de monomère utilisé comme solvant va de 2,5 à 80% en poids des monomères totaux.

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10. Procédé suivant la revendication 9, dans lequel la proportion de monomère utilisé comme solvant va de 7 à 50% en poids des monomères totaux.

11. Revêtement ou film obtenu à partir d'une dispersion préparée par le procédé suivant l'une quelconque des revendications 1 à 10.

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12. Article composite qui comprend un film suivant la revendication 11 comme couche d'adhésif.

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Description

This invention relates to aqueous dispersions and more particularly to aqueous polymer dispersions containing a water-dispersible polyurethane and a vinyl polymer.

5 Aqueous polyurethane dispersions are well known and are used, for example, in the production of coatings and films. Dispersion of the polyurethane in the aqueous system has been achieved by the use either of external surfactants or by including appropriate ionic or nonionic groups in the polyurethane to render it self-dispersible. Thus, for example, U.S. Pat. No. 4066591 describes aqueous dispersions obtained by dispersing an isocyanate-terminated polyurethane prepolymer which contains anionic salt groups in an 10 aqueous medium and then reacting the dispersed prepolymer with an active hydrogen containing chain extender.

It has also been proposed to modify the properties of polyurethane dispersions by including vinyl polymers therein. Several patents, for example U.S. Pats Nos. 3705164, 4198330 and 4318833, describe processes wherein the vinyl polymer is formed *in situ* by polymerising one or more vinyl monomers in the 15 presence of an aqueous dispersion of a polyurethane containing anionic salt groups. In some cases, the polyurethane prepolymer is formed in the presence of, or subsequently diluted with, an organic solvent which serves to reduce the viscosity of the prepolymer and/or facilitate its dispersion in water. The solvent may then be removed from the dispersion by distillation as described in US 3705164, a troublesome procedure, or allowed to remain as described in US 4318833 and possibly adversely affect the final product 20 and/or the environment.

In the process described in EP-A-189945, the polyurethane prepolymer is formed in the presence of vinyl monomer, thereby avoiding the need for conventional solvents. The solution of prepolymer is then dispersed in water, the prepolymer is chain extended and the vinyl monomer is subjected to suspension polymerisation using conventional free radical catalysts. However, this procedure is not entirely satisfactory, 25 the hydrophobicity of some prepolymers and vinyl monomers being such that unstable or gelled dispersions are formed. Additionally, in the production of copolymers, no control over the copolymer composition distribution can be achieved because of the batch nature of the polymerisation process. This is a particular problem when the comonomer reactivity ratios are not well matched.

It has now been found that superior dispersions may be obtained by forming an aqueous dispersion of 30 a solution of a prepolymer containing anionic groups in a selected amount of vinyl monomer (sufficient to provide viscosities suitable for the production of good dispersions) and then polymerising the monomer, either by free radical polymerisation following the addition of further monomer, or by conventional emulsion polymerisation techniques with further addition of monomer during the emulsion polymerisation. Furthermore, it has been found that no additional surfactant is required either at the prepolymer dispersion stage or 35 during polymerisation of the vinyl monomer.

Accordingly, the invention provides a process for the preparation of a surfactant free aqueous polymer dispersion containing an anionic water-dispersible polyurethane and a vinyl polymer in a weight ratio of from 10:90 to 90:10, said process comprising:

- 40 A) forming a solution of an anionic water-dispersible isocyanate-terminated polyurethane in at least one vinyl monomer;
- B) dispersing the solution in an aqueous medium;
- C) chain extending the polyurethane, and subsequently either
- D) adding further vinyl monomer
- 45 and
- E) initiating polymerisation of the vinyl monomer,
- or
- F) initiating polymerisation of the vinyl monomer,
- and
- 50 G) adding further vinyl monomer during polymerisation.

Preferred dispersions made from the process contain the anionic water-dispersible polyurethane and the vinyl polymer in a weight ratio of from 20:80 to 80:20.

55 The anionic water-dispersible isocyanate-terminated polyurethane will be a polyurethane prepolymer having acidic residues providing water-dispersibility. Such prepolymers and methods for their preparation have been fully described in the prior art.

Polyurethane prepolymers having acidic centres include isocyanate-terminated reaction products of:

- i) an organic polyisocyanate;
- ii) a polymeric polyol having a molecular weight of from 500 to 6000;

- iii) an isocyanate-reactive compound having at least one acid group and at least two groups that are more reactive than the acid group towards isocyanates, and, optionally
- iv) a low molecular weight polyol having a molecular weight below 500.

The polyisocyanate used in making the prepolymer may be an aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanate. Examples of suitable polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-xylylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene, diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, polymethylene polyphenyl polyisocyanates and 1,5-naphthylene diisocyanate. Mixtures of polyisocyanates can be used and 10 also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Polymeric polyols having molecular weights in the range of 500-6000 which may be used in the preparation of the prepolymer particularly include diols and triols and mixtures thereof but higher functionality polyols may be used, for example as minor components in admixture with diols. The polyols may 15 be members of any of the chemical classes of polymeric polyols used or proposed to be used in polyurethane formulations. In particular, the polyols may be polyesters, polyesteramides, polyethers, polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes. Preferred polyol molecular weights are from 700 to 3000.

Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric 20 alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, furan dimethanol, cyclohexane dimethanol, glycerol, trimethylolpropane or pentaerythritol, or mixtures thereof, with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their methyl esters, phthalic anhydride or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a 25 polyol may also be used. Polyesteramides may be obtained by the inclusion of amino-alcohols such as ethanolamine in polyesterification mixtures.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide or tetrahydrofuran or by the addition of one or more such 30 oxides to polyfunctional initiators, for example water, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol or Bisphenol A. Especially useful polyesters include polyoxypolypropylene diols and triols, poly (oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to appropriate initiators and polytetramethylene ether glycols obtained by the polymerisation of tetrahydrofuran.

Polythioether polyols which may be used include products obtained by condensing thiodiglycol either 35 alone or with other glycols, dicarboxylic acids, formaldehyde, aminoalcohols or aminocarboxylic acids.

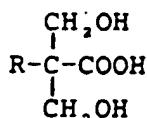
Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Polyacetal polyols which may be used include those prepared by reacting glycols such as diethylene 40 glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo and copolymers.

Polyols having molecular weights below 500 which may optionally be used in the preparation of the prepolymer particularly include diols and triols and mixtures thereof but higher functionality polyols may be 45 used. Examples of such lower molecular weight polyols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis (hydroxyethyl) terephthalate, cyclohexane dimethanol, furan dimethanol, glycerol and the reaction products, up to molecular weight 499, of such polyols with propylene oxide and/or ethylene oxide.

Isocyanate-reactive compounds containing acid groups which may be used in the preparation of 50 prepolymers having acidic centres include carboxy group containing diols and triols, for example dihydroxy alkanic acids of the formula:



wherein R is hydrogen or alkyl. The preferred carboxy containing diol is 2,2-dimethylolpropionic acid. If desired, the carboxy containing diol or triol may be incorporated into a polyester by reaction with a dicarboxylic acid before being incorporated into the prepolymer. Useful materials include the fumarate polyether glycols described in US 4460738. Other useful acid group containing compounds include amino carboxylic acids, for example lysine, cystine and 3,5-diaminobenzoic acid and sulphonic acids, for example 4,6-diaminobenzene-1,3-disulphonic acid.

5 The anionic water-dispersible isocyanate-terminated polyurethane prepolymer may be prepared in conventional manner by reacting a stoichiometric excess of the of the organic polyisocyanate with the polymeric polyol having a molecular weight in the range 500 to 6000 and the other required isocyanate-reactive compounds under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until reaction between the isocyanate groups and the hydroxyl groups is substantially complete. The polyisocyanate and the active hydrogen containing components are suitably reacted in such proportions that the ratio of number of isocyanate groups to the number of hydroxyl groups is in the range from about 1.1:1 to about 6:1, preferably within the range of from 1.5:1 to 3:1. If desired, catalysts such as 10 dibutyltin dilaurate and stannous octoate may be used to assist prepolymer formation.

10 The solution of the water-dispersible polyurethane prepolymer in vinyl monomer may be produced by adding one or more vinyl monomers to the prepolymer or, preferably by forming the prepolymer in the presence of one or more vinyl monomers.

15 Suitable vinyl monomers in which the prepolymer may be dissolved contain one or more polymerisable ethylenically unsaturated groups. Preferred monomers are liquid under the temperature conditions of prepolymer formation although the possibility of using solid monomers in conjunction with organic solvents is not excluded. It is also preferred to use monomers which do not contain isocyanate or isocyanate-reactive groups.

20 Thus, suitable monomers include ethylenically unsaturated hydrocarbons, esters and ethers, especially esters of acrylic and methacrylic acids, esters and ethers of vinyl alcohol and styrene. Specific examples include butadiene, isoprene, styrene, substituted styrenes, the lower alkyl (C1-6) esters of acrylic, methacrylic and maleic acids, vinyl acetate, butyrate, acrylate and methacrylate, acrylonitrile, allyl methacrylate, vinyl methyl, propyl and butyl ethers, divinyl ether, divinyl sulphide, vinyl chloride, vinylidene chloride, hexanediol diacrylate, trimethylolpropane triacrylate and the like. Free acids should not be 25 employed since they may destabilise the dispersion.

25 The prepolymer/vinyl monomer solution may be dispersed in water using techniques well known in the art. Preferably, the solution is added to the water with agitation or, alternatively, water may be stirred into the solution.

30 The active hydrogen containing chain extender which is reacted with the prepolymer is suitably a polyol, an amino alcohol, ammonia, a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic amine especially a diamine, hydrazine or a substituted hydrazine. Water-soluble chain extenders are preferred, and water itself may be effective.

35 Examples of suitable chain extenders useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, 40 piperazine, 2-methyl piperazine, phenylene diamine, tolylene diamine, xylylene diamine, tris (2-aminoethyl) amine, 3,3'-dinitrobenzidine, 4,4'-methylenebis (2-chloraniline), 3,3'-dichloro-4,4'-bi-phenyl diamine, 2,6-diaminopyridine, 4,4'-diaminodiphenylmethane, menthane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolyzed products. Also materials such as hydrazine, azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, hydrazides of dicarboxylic acids and sulfonic acids such as 45 adipic acid mono- or dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, tartaric acid dihydrazide, 1,3-phenylene disulfonic acid dihydrazide omega-amino-caproic acid dihydrazide, hydrazides made by reacting lactones with hydrazine such as gamma-hydroxylbutyric hydrazide, bis-semi-carbazide, bis-hydrazide carbonic esters of glycols such as any of the lycols mentioned above.

50 Where the chain extender is other than water, for example a diamine or hydrazine, it may be added to the aqueous dispersion of prepolymer and vinyl monomer or, alternatively, it may already be present in the aqueous medium when the prepolymer and monomer are dispersed therein.

55 The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5° to 95°C or more, preferably from about 10° to about 45°C.

55 The amount of chain extender employed should be approximately equivalent to the free-NCO groups in the prepolymer, the ratio of active hydrogens in the chain extender to NCO groups in the prepolymer preferably being in the range from 0.7 to 2.00:1. Of course when water is employed as the chain extender, these ratios will not be applicable since the water, functioning both as chain extender and dispersing

medium, will be present in a gross excess relative to the free-NCO groups.

The conversion of any acid groups present in the prepolymer to anionic groups may be effected by neutralising the said acidic groups before, after or simultaneously with formation of the aqueous dispersion. Suitable neutralising agents include tertiary amines such as triethylamine.

5 Polymerisation of the vinyl monomer or monomers may be effected by one of two methods.

In the first method, additional monomer (the same or different vinyl monomer or monomer mixture) is added and may swell the polyurethane. The monomer may then be polymerised using a conventional free radical initiator system. The proportion of monomer used as solvent for the prepolymer is suitably from 1.5 to 95%, preferably from 2.5 to 80% and more preferably from 7 to 50% by weight of the total monomers.

10 In the second method, polymerisation of the vinyl monomer diluent and feeding of the same or a different vinyl monomer or monomer mixture is allowed to continue until complete. The proportion of monomer used as solvent for the prepolymer may be as indicated for the first method.

In either method of polymerisation, the vinyl monomers which may be added and polymerised include those mentioned above. Functional monomers such as hydroxylalkyl acrylates and methacrylates may also 15 be incorporated at this stage since the free isocyanate groups of the prepolymer will have reacted with the chain extender.

Suitable free radical initiators include mixtures partitioning between the aqueous and organic phases, for example a combination of t-butyl hydroperoxide, isoascorbic acid and Fe.EDTA.

20 The aqueous polymer dispersions produced by the method of the invention are stable for long periods of time despite the absence of emulsifiers. If desired, minor amounts of solvents may be included in the dispersions.

The dispersions obtained by the method of the invention may be employed as coating compositions and may be applied to any substrate including wood, metals, glass, cloth, leather, paper, plastics, foam and the like, by a conventional method including brushing, dipping, flow coating, spraying and the like. Films 25 obtained from the coating compositions may be used as adhesives in the production of composite articles.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

Example 1

30

A prepolymer solution was prepared from the following ingredients:

	Parts
35	Isophorone diisocyanate 33.9
	Dimethylolpropionic acid 6.0
	Polycarbonate diol 58.9
	Trimethylolpropane 0.6
40	Cyclohexane dimethanol 0.6
	Methyl methacrylate 42.8

The prepolymer solution was then neutralised with triethylamine, dispersed in water and extended with ethylene diamine using no surfactant.

45 A monomer mixture containing 97.2 parts of methyl methacrylate and 93 parts of butyl acrylate was added to the polyurethane dispersion and swollen in.

Polymerisation was effected using t-butyl hydroperoxide and isoascorbic acid.

The resulting polymer dispersion was translucent, had a low viscosity and contained a small amount of sediment.

50

Example 2

A polyurethane dispersion was prepared as described in Example 1. Polymerisation was initiated using t-butylhydroperoxide and isoascorbic acid. During polymerisation, a monomer mixture containing 97.2 parts of methyl methacrylate and 93 parts of butyl acrylate was fed in.

55 The resulting polymer dispersion was again translucent, of low viscosity and had a low sediment content.

Comparative Example C1

A prepolymer solution was prepared from the following ingredients:

	Parts
5	
	Isophorone diisocyanate 33.9
	Dimethylopropionic acid 6.0
	Polycarbonate diol 58.9
	Trimethylopropane 0.6
	Cyclohexane dimethanol 0.6
10	
	Methyl methacrylate 140
	Butyl acrylate 93

The prepolymer solution was then neutralised with triethylamine, dispersed in water to 35% solids (including monomer) and extended with ethylene diamine.

15 The product was a white hazy dispersion with coarse particle size and heavy sediment. Phase separation occurred after 3 days.

Initiation with t-butyl hydroperoxide and isoascorbic acid after 1 day resulted in coagulation at the start of the polymerisation.

20 Example 3

A. Polyurethane preparation

25 The urethane prepolymer was prepared in a fourneck round bottom flask, equipped with a thermometer, mechanical stirrer, condenser, dry air or nitrogen blanket and heating mantle, by using the following formulation:

	Parts
30	
	Isophorone diisocyanate 525.00
	Terathane-1000 (OH number - 114.3mg KOH/g) 635.33
	Dimethylopropionic acid 81.25
	1,4-Cyclohexane dimethanol 8.43
35	
	Catalyst: dibutyltinlaurate 0.15
	Butyl acrylate 313.85
	Inhibitor:Topanol O 0.63

Half of the dibutyltinlaurate was added before heating the mixture of diisocyanate and polyols and the other part after 1 hour at reaction temperature. 139.56 parts of the butyl acrylate were added before reaction, the remaining parts were used for diluting the prepolymer after the reaction. The inhibitor was equally divided over the butyl acrylate. Total reaction time took 2 hours, the reaction temperature was maintained at 90-95 °C. The residual NCO content was 5.59% (theoretical 5.64%).

45 The prepolymer was neutralized by mixing in 60.13 parts triethylamine at 50-60 °C for half an hour. The neutralized prepolymer was dispersed in 3071.69 parts of demineralized water during 60 minutes. After dispersion, 44.17 parts hydrazine monohydrate were added to chain extend the NCO terminated prepolymer. The resulting polyurethane dispersion had a pH of 7.8, a Brookfield viscosity at 25 °C of 37mPas and solids content of 27.3%.

(Terathane 1000 is a polytetramethylene glycol)

50 B. Urethane vinyl polymer preparation

The radical polymerisation for producing the polymer dispersion having a urethane-acrylic polymer ratio of 40/60 was carried out using the following process:

55 In similar equipment under a nitrogen blanket were charged 1136.19 parts of the dispersion 508.66 parts demineralized water and 2.25 parts of tert. butyl hydroperoxide. To this dispersion were added 10% of the monomer feed listed below and 9 parts of a 2% i-ascorbic acid solution in water. (neutralized with ammonia to pH 7-9). After heating to 75 °C, the remaining monomer feed was added over 60 minutes. Th

temperature was maintained at $75 \pm 2^\circ\text{C}$ for 75 minutes. After the i-ascorbic acid feed was completed, the reaction medium was brought to $80\text{--}82^\circ\text{C}$ for half an hour post-reaction before cooling.

5		Monomer feed:	
			Parts
		Methyl methacrylate	301.95
10		Butyl Methacrylate	58.05
		Butyl acrylate	15.00
		Dimethyl ethanol amine	0.45

The obtained polyurethane-acrylic monomer showed the following specification; free monomer content of 0.02%, 0.14% sediment, pH of 8.0, a Brookfield viscosity at 25°C of 160 mPas and contained 37.5% solids. The minimum film forming temperature was lower than 20°C . The end product had a blue white, nearly translucent appearance, the measured absorbance by spectrometry at 650nm using a path length of 1mm was 5.1. Some increase of viscosity was noticed after 4 weeks storage test at 50°C . The film cast on a glass plate with film thickness of 30 μm dry showed a könig hardness of 136 sec. Ethanol and methyl ethyl ketone double rubs were 43x and 155x respectively.

20 Example 4

A. Polyurethane preparation

25 Preparation of a polyurethane dispersion was by a procedure similar to that of Example 3, the prepolymer being based on polycarbonate diol and a triol and methyl methacrylate being used as reactive diluent.

30		Prepolymer components:	
			Parts
		Isophorone diisocyanate	536.32
35		Permanol KM-10-122 (OH = 55.49mg KOH/g)	930.68
		Dimethylolpropionic acid	94.80
		Trimethylolpropane	9.48
		1,4-cyclohexane dimethanol	8.89
		dibutyltinlaurate catalyst	0.19
40		Methyl methacrylate	678.21
		Topanol O inhibitor	1.36

The prepolymer reaction took 3 hours. The 90% solution in methyl methacrylate was further diluted till 80% and 70% after 1 and 2 hours reaction time.

45		Components for preparing the polyurethane dispersion.	
			Parts
		Prepolymer	685.71
50		Triethylamine	21.28
		Demineralized water	1260.02
		Ethylene diamine	20.73

The low viscous translucent urethane dispersion contained 25.3% solids, <0.02% sediment was found.

55 B Urethane vinyl polymer preparation

Components:	
	Parts
5	Polyurethane dispersion 372.70
	Demineralized water 265.87
	Tert. butylhydroperoxide 1.31
	iso-ascorbic acid solution 1% in water 63.80
10	Methyl methacrylate 87.43
	Butyl acrylate 84.00
	Dimethyl ethanolamine 0.21
	The urethane vinyl polymer ratio was 30/70.

Specifications:	
15	Solids 34.3%
	pH 7.7
20	viscosity at 25 °C 10 mPas
	sediment <0.02%
	appearance blue-white
	Absorbance (at 650nm) 31
25	minimum film forming temperature <15 °C

Film properties:	
30	König hardness 78 sec
	Ethanol double rub 18x
	MEK double rub 48x

35 Example 5

A polyurethane vinyl polymer was prepared using a urethane dispersion and other components in the recipe for the radical polymerization as described in Example 4.

However, the radical polymerization procedure was as follows:

First addition of the monomer blend to the diluted polyurethane dispersion, followed by addition of tert. butyl hydroperoxide and 10% of the iso-ascorbic acid solution.

Further feeding of the iso-ascorbic acid solution at 40 °C resulted in an exothermic reaction, causing a peak temperature at 79 °C. After 30 minutes feeding time and 30 minutes post-reaction at 80-82 °C, a free monomer content was found at 0.02%

Other specifications are	
45	Solids 34.3%
	pH 7.9
50	Viscosity at 25 °C 10 mPas
	Sediment <0.02%
	Appearance blue-white
	Absorbance 24
55	minimum film forming temperature 23 °C
	The urethane vinyl ratio was 30/70.

Comparative Example C2

The polyurethane prepolymer, described in Example 4, was diluted with methyl methacrylate and butyl acrylate so that the final urethane vinyl polymer ratio should become 30/70. the recipe for dispersing this prepolymer was as follows:

5

	Parts:
Polyurethane prepolymer	285.71
Methyl methacrylate	194.29
Butyl acrylate	186.67
Triethylamine	8.87
Demineralised water	1245.27
Ethylenediamine	8.64

10

Neutralising, dispersing and chain extending the prepolymer-monomer blend resulted in a hazy white mixture with a coarse particle size and much sediment. Solids including the monomers was 35%. Phase separation occurred after 3 days.

This product was subjected to a radical polymerization after 1 day. First adding the tert. butyl-hydroperoxide and feeding the iso-ascorbic acid at 40°C did not result in an exothermic reaction; heating to 60°C also did not result in an exothermic reaction. Finally, the mixture gelled after 75 minutes reaction time.

Example 6

A. Polyurethane preparation

The procedure was identical to Example 3. However, the urethane polymer, was modified with a triol and a tetra functional amine. The prepolymer was prepared in presence of 134.63 parts of butyl acrylate. The residual butyl acrylate and acrylonitrile were used for dilution after completing the prepolymer reaction, but before the dispersion step. Ethylene diamine and triethylene tetramine were used as extension agents.

30

Prepolymer components:	
	parts:
Isophorone diisocyanate	512.69
Terathane-1000 (OH = 114.3 mg KOH/g)	595.80
Dimethylol propionic acid	78.00
Trimethylol propane	13.51
dibutyltinlaurate catalyst	0.14
Butyl acrylate	150.74
Acrylonitrile	150.74
Inhibitor Topanol O	0.60

The prepolymer contained 5.16% NCO (theoretical 5.73%).

45

Components for preparing the polyurethane dispersion.

50

	parts:
Prepolymer	1502.22
Triethylamine	57.73
Demineralized water	3416.47
Ethylene diamine	51.39
Tri ethylene tetra amine	6.42

55

The polyurethane dispersion showed a translucent appearance. The solids content was 25%.

B. Urethane vinyl polymer preparation

According to the procedure described in Example 3, the following components were used for the polymerization:

		parts:
5	polyurethane dispersion	670.24
	Demineralized water	203.36
10	Tert. butyl hydroperoxide	1.50
	Iso-ascorbic acid solution, 1% in water	72.75
	Butyl acrylate	52.00
	Methyl methacrylate	84.00
	Acrylonitrile	52.00
15	Allyl methacrylate	12.00
	Dimethyl ethanol amine	0.24

Since 0.60% free monomer was still present, a post-reaction with ammonium persulphate was necessary.

Therefore, 4.67 g of a 10% ammonium persulphate solution (neutralized with ammonia to pH 8) was added and the reaction mixture was heated to 90-92°C and held at this temperature for half an hour before cooling. The free monomer content was then 0.06%.

The polyurethane-vinyl polymer ratio was 40/60.

The specification of the resulting dispersion was as follows:

25	solids	35.2%
	pH	8.0
	viscosity at 25°C	600 mPas
30	sediment	0.30%
	minimum film forming temperature	16°C
	appearance	blue white
35	absorbance (at 650 nm)	31

The storage stability at 50°C was insufficient, in the third week the polymer gelled. However, at ambient temperature, the dispersion was stable for more than one year.

	Film properties:	
40	König hardness	144 sec
	Ethanol double rub	15x
	MEK double rub	20x

Example 7

This Example describes the preparation of a urethane-vinyl polymer with the same polyurethane dispersion, same components in the same ratios and a comparable radical polymerization as in Example 6, but a sequential monomer feed was used for introducing acrylonitrile in the first and 90% of the allyl methacrylate in the second feed.

50

55

EP 0 308 115 B1

Recipe for the radical polymerization:	
	Parts:
5	Polyurethane dispersion 670.24
	Demineralized water 203.36
	Tert butyl hydroperoxide 1.50
	Iso ascorbic acid solution, 1% in water 72.75
First monomer feed:	
10	Butyl acrylate 30.40
	Methyl methacrylate 58.80
	Acrylonitrile 52.00
	Allyl methacrylate 1.20
	Dimethyl ethanol amine 0.17
Second monomer feed:	
15	Butyl acrylate 21.60
	Methyl methacrylate 25.20
	Allyl methacrylate 10.80
	Dimethyl ethanol amine 0.07
The urethane-vinyl ratio was 40/60.	
The ratio first/second monomer feed was 70/30.	

25

Specification:	
solids	35.1%
pH	8.5
viscosity at 25 °C	111 mPas
sediment	0.08%
free monomer	0.02%
minimum film forming temperature	16 °C
appearance	blue white
absorbance (at 650 nm)	25
storage stability at 50 °C, for 4 weeks	OK

40

Film properties:	
König hardness	135 sec
Ethanol double rub	20x
MEK double rub	31x

45

Example 8

50 Polyurethane-vinyl polymer based on the polyurethane dispersion as mentioned in Example 3, the acrylic part being modified with styrene. The urethane-vinyl polymer ratio was 50/50.

65

EP 0 308 115 B1

Recipe for the radical polymerization:	
	parts:
5	Polyurethane dispersion (30.0% solids) 1340.20
	Demineralized water 245.75
	Tert butyl hydroperoxide 2.46
	Iso-ascorbic acid solution, 1% in water 116.78
10	Styrene 141.51
	Methyl methacrylate 117.92
	Acrylonitrile 35.38

Specification:	
15	solids 35.4%
	pH 8.0
	viscosity at 25 °C 19 mPas
20	sediment 0.02%
	free monomer 0.40%
	minimum film forming temperature < 15 °C
	absorbance (at 650 nm) 19
	appearance blue white

Film properties:	
30	König hardness 101 sec
	Ethanol double rub 10x
	MEK double rub 10X

Example 9

35 Polyurethane vinyl polymer based on the polyurethane dispersion as described in Example 3, the acrylic part modified with styrene as in Example 8, but with a polyurethane-vinyl polymer ratio of 20/80.

Recipe for the radical polymerization:	
	Parts:
40	Polyurethane dispersion (30.0% solids) 496.72
	Demineralized water 778.30
45	Tert butylhydroperoxide 3.64
	Iso-ascorbic acid solution, 1% in water 175.00
	Styrene 209.79
	Methyl methacrylate 174.83
	Acrylonitrile 52.45
50	Butyl acrylate 109.24

Specification:	
5	Solids 35.7%
	pH 7.7
	Viscosity at 25 °C 16 mPas
10	Sediment 0.03%
	Free monomer 0.25%
	Minimum film forming temperature 43 °C
	Absorbance 31
	Appearance blue-white

Film properties:	
15	König hardness 180 sec
	Ethanol double rub 30x
	MEK double rub 30x

20 Example 10

A. Polyurethane preparation

25 A polyesterdiol based polyurethane was prepared following the procedure of Example 1. The prepolymer was diluted with the butyl acrylate-Topanol O solution, but not until the prepolymer preparation was finished.

Prepolymer components		
	Parts:	
30	Isophorone diisocyanate 1561.44	
	Ruco S-1063-120 polyester (OH = 116.7 mg KOH/g) 1542.33	
35	Dimethylol propionic acid 218.24	
	1,4-Cyclohexane dimethanol 38.68	
	dibutyltinlaurate catalyst 0.40	
	Butyl acrylate 839.77	
	Topanol O inhibitor 1.68	
40	The prepolymer contained 6.51% NCO (7.04% NCO theoretical).	

Recipe for preparing the polyurethane dispersion:	
45	Prepolymer 3200.00
	Triethylamine 123.00
	Demineralized water 5523.33
	Ethylene diamine 134.14

50

55

5

Specification of polyurethane dispersion:	
Solids	26.0%
pH	7.5
Viscosity at 25 °C	28 mPas
Sediment	0.08%
Appearance	blue-white

10

B. Urethane-vinyl polymer preparation

Radical polymerization was according to the procedure of Example 3. However, the iso-ascorbic acid reducing agent was replaced by sodium sulphoxylate formaldehyde.

15 The following recipe was used:

20

		Parts:
Polyurethane dispersion		1067.41
Demineralized water		455.06
Tert butylhydroperoxide		2.62
Sodium sulphoxylate formaldehyde, 1% in water		126.00
Methyl methacrylate		280.94
Butyl methacrylate		54.01
Butyl acrylate		13.96

25

The urethane-vinyl polymer ratio was 40/60.

30

Specification:	
Solids	34.6%
pH	8.1
Viscosity at 25 °C	9 mPas
Sediment	0.10%
Free monomer	0.12%
Minimum film forming temperature	39 °C
Absorbance (at 650 nm)	56
Appearance	hazy, white

40

45

Film properties:	
König hardness	163 sec
Ethanol double rub	30x
MEK double rub	120x

50

Example 11

A. Polyurethane preparation

55 A polycaprolactonediol and 4,4'-methylene bis (cyclohexyl) diisocyanate based polyurethane was prepared as described in Example 3. Butyl acrylate and the catalyst were added before starting the prepolymer preparation. The reaction temperature was held at 80-85 °C for 2 hours.

5

Prepolymer components	
	Parts:
4,4'-methylene bis (cyclohexyl) diisocyanate	597.36
Polycaprolactonediol (OH = 92.7 mg KOH/g)	846.64
Dimethylol propionic acid	76.00
dibutyltinlaurate catalyst	0.58
Butyl acrylate	379.40
Topanol O inhibitor	0.75

10

The prepolymer contained 4.20% NCO (theoretical 4.42%).

15

Recipe for preparing the urethane dispersion:	
	Parts:
Prepolymer	600.00
Triethylamine	17.34
Demineralized water	1405.54
Hydrazine monohydrate	13.90

20

25

Specification of polyurethane dispersion:	
Solids	23.5%
pH	8.6
Sediment	< 0.02
Viscosity at 25 °C	36 mPas
Appearance	colourless,translucent

30

B. Urethane-vinyl polymer preparation

35 Radical polymerization according to Example 3.

40

Recipe:	
	Parts:
Polyurethane dispersion	1412.40
Demineralized water	213.73
Tert butylhydroperoxide	2.21
Iso-ascorbic acid, 1% solution in water	106.00
Methyl methacrylate	258.58
Butyl methacrylate	7.08

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The urethane-vinyl polymer was 50/50.

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EP 0 308 115 B1

Specification:	
5	Solids 33.5%
	pH 8.0
	Viscosity at 25 °C 17 mPas
	Sediment < 0.02%
10	Free monomer 0.11%
	Minimum film forming temperature 31 °C
	Absorbance 7.7
	Appearance blue-white

Film properties:	
15	König hardness 150 sec
	Ethanol double rubs 140x
	MEK double rubs > 200x

20 Example 12

A. Polyurethane preparation

25 Polyurethane based on toluene diisocyanate (80/20 ratio for the 2.4 and 2.6 isomers) and diphenylmethane diisocyanate (75/25 ratio for the 4.4' and 2.4' isomers).

Recipe for prepolymer preparation:	
	Parts:
30	Toluene diisocyanate 246.00
	Diphenylmethane diisocyanate 246.00
	Terathane-1000 polyetherdiol (OH = 114.3 mg KOH/g) 579.24
35	1,4-Cyclohexane dimethanol 8.76
	Dimethylol propionic acid 120.00
	Butyl acrylate 133.33
	Methyl methacrylate 266.67
	Styrene 400.00
40	Topanol O inhibitor 1.60

45 The urethane prepolymer was prepared by first feeding the polyetherdiol and 1,4-cyclohexyl dimethanol blend to the diisocyanate solution in 1 hour and maintaining the reaction temperature at 50-55 °C. The procedure was continued by the addition of dimethylol propionic acid in 1 hour while keeping the temperature at 55-60 °C. The reaction mixture was held at 55-60 °C for another 6 hours and 2 hours at 65-70 °C. In the meantime, the mixture was diluted with butyl acrylate, methyl methacrylate and styrene after 3, 9 and 10 hours reaction time. The NCO content was then 3.73%. (Theoretical 3.25%).

50 The urethane dispersion was prepared by the addition of 400.00 parts prepolymer in 1 hour to an aqueous phase which contain 26.05 parts triethyl amine, 1.04 parts hydrazine and 841.18 parts water. The residual 0.35 parts hydrazine were simultaneously fed, also in 1 hour at ambient temperature.

Specification of polyurethane dispersion:	
Solids	24.1%
pH	8.2
Viscosity at 25 °C	900 mPas
Sediment	0.04%
Absorbance	19
Appearance	blue-white

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B. Urethane-vinyl polymer preparation

Radical polymerization following the procedure described in Example 3.

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Recipe:	
	Parts:
Polyurethane dispersion	851.75
Demineralized water	309.62
Tert butyl hydroperoxide	1.25
Iso ascorbic acid, 1% solution in water	60.00
Styrene	88.60
Methyl methacrylate	15.56
Acrylonitrile	18.00
Butyl acrylate	11.10

The urethane-vinyl polymer ratio was 50/50.

Specification:	
Solids	30.1%
pH	8.1
Viscosity at 25 °C	29 mPas
Sediment	0.40%
Free monomer	0.20%
Absorbance	143
Appearance	slightly hazy, white-yellow

45

Film properties:	
König hardness	136 sec
Ethanol double rub	> 200x
MEK double rub	80x

50 Example 13

A. Polyurethane preparation

The urethane polymer was prepared by a procedure similar to that of Example 3, but was modified with 55 ethylene diamine and a tetra functional amine. The 90% prepolymer in butyl acrylate was further diluted to 80% after the prepolymer preparation:

5

Prepolymer components:	
	Parts:
Isophorone diisocyanate	672.00
Terathane-1000 polyether (OH = 114.3 mg KOH/g)	813.22
Dimethylol propionic acid	104.00
1,4-Cyclohexane dimethanol	10.78
dibutyltinlaurate catalyst	0.20
Butyl acrylate	400.00
Topanol O inhibitor	0.80

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The prepolymer contained 5.42% NCO. (Theoretical 5.64%).

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Recipe for preparing the polyurethane dispersion:	
	Parts:
Prepolymer	600.00
Triethylamine	23.08
Demineralized water	1212.89
Ethylene diamine	19.13
Triethylene tetramine	2.39

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Specification of polyurethane dispersion:	
Solids	27.5%
pH	7.7
Viscosity at 25 °C	27
Sediment	>0.02%
Absorbance (at 650 nm)	2.1
Appearance	translucent

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B. Urethane-vinyl polymer preparation

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Radical polymerization based on azo-bis (isobutyronitrile) initiator. Diallyl phthalate was incorporated as difunctional component.

The procedure was as follows:

The monomer blend including the initiator were fed to the diluted polyurethane dispersion for 1 hour, keeping the reaction temperature at 80 ± 2 °C. After half an hour postreaction at 90 ± 2 °C, a free monomer content was found of 0.02%.

45

Recipe for radical polymerization:	
	Parts:
Urethane dispersion	483.73
Demineralized water	162.24
Azo-bis (isobutyronitrile)	0.75
Butyl acrylate	2.24
Butyl methacrylate	12.50
Methyl methacrylate	78.39
Diallyl phthalate	0.63

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The urethane-vinyl polymer ratio was 50/50.

Specification:	
Solids	32.3%
pH	8.6
Viscosity at 25 °C	82
Sediment	1.0%
Free monomer	0.02%
Absorbance (at 650 nm)	18
Appearance	blue-white

5

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Example 1415 A. Polyurethane preparation

Urethane polymer based on Terathane-2000 polyether diol and 4,4'-methylene bis (cyclohexyl) diisocyanate, prepared as described in Example 3. The catalyst was totally added before and methyl methacrylate was added after finishing the prepolymer preparation.

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Prepolymer components:	
	Parts:
4,4'-Methylene bis (cyclohexyl) diisocyanate	1266.15
Terathane 2000 polyetherdiol (OH = 56.7 mg KOH/g)	1693.85
Dimethyl propionic acid	240.00
dibutyltinlaurate catalyst	1.23
Methyl methacrylate	799.98
Topanol O inhibitor	1.60

30 The prepolymer contained 4.36% NCO (theoretical 4.47%).

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Recipe for preparing the polyurethane dispersion:	
	Parts:
Prepolymer	3100.00
Triethylamine	138.97
Deminerlized water	6403.72
Hydrazine monohydrate	71.69

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Specification of the polyurethane dispersion:	
Solids	26.1
pH	8.3
Viscosity at 25 °C	19mPas
Sediment	0.02%
Absorbance (at 650 nm)	0.1
Appearance	clear, colourless

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B. Urethane-vinyl polymer preparation

The radical polymerization, with a urethane-vinyl polymer ratio of 70/30 was carried out as follows:

A dimethyl ethanol amine (DMEA) neutralized mixture of 0.34 parts tert butyl hydroperoxide and 22.90 parts demineralized water (pH = 8.0) was blended with 500 parts of above described urethane dispersion in

the reactor. 0.17 parts isoascorbic acid dissolved in 17.00 parts demineralized water was neutralized with DMEA till pH = 8.0. 10% of this mixture was added to the reactor phase. The reaction mixture was heated till 85°C. When the reaction mixture reached 75°C the monomer feed was started. Total feed-time for the monomer mixture was 15 minutes. At the same time with the monomer feed the remaining isoascorbic acid solution was fed in. This feed lasted for 30 minutes. After completion of this, the mixture was kept at 85°C for another 30 minutes after which the reactor was stripped at 85°C for 30 minutes.

5 The specification of the 70/30 urethane/acrylate dispersion was as follows:

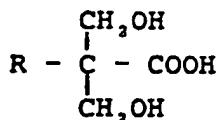
10	Solids	33.0
	pH	7.7
	Viscosity at 25°C	30
	Sediment	< 0.02%
15	Minimum film forming temperature	< 15
	Appearance	blue-white

[The words Terathane, Permanol, Ruco and Topanol used herein are known to be registered trade marks.]

20 **Claims**

1. A process for the preparation of a surfactant-free aqueous polymer dispersion containing an anionic water-dispersible polyurethane and a vinyl polymer in a weight ratio of from 10:90 to 90:10, said process comprising:
 - (A) forming a solution of an anionic water-dispersible isocyanate-terminated polyurethane in at least one vinyl monomer;
 - (B) dispersing the solution in an aqueous medium;
 - (C) chain extending the polyurethane, and subsequently either
 - (D) adding further vinyl monomer, and
 - (E) initiating polymerisation of the vinyl monomer, or
 - (F) initiating polymerisation of the vinyl monomer, and
 - (G) adding further vinyl monomer during polymerisation.
2. A process according to claim 1, wherein the dispersion formed contains the water-dispersible polyurethane and the vinyl polymer in a weight ratio of from 20:80 to 80:20.
3. A process according to claim 1 or claim 2 wherein the anionic water-dispersible isocyanate-terminated polyurethane is a reaction product of:
 - (i) an organic polyisocyanate;
 - (ii) a polymeric polyol having a molecular weight of from 500 to 6000;
 - (iii) an isocyanate-reactive compound having at least one acid group and at least two groups that are more reactive than the acid group towards isocyanates, and, optionally
 - (iv) a low molecular weight polyol having a molecular weight below 500.
- 45 4. A process according to any preceding claim wherein the isocyanate-reactive compound having at least one acid group is a carboxy group containing diol or triol
5. A process according to claim 4 wherein the carboxy group containing diol or triol is a dihydroxy alkanoic acid of the formula:

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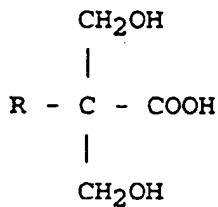
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wherein R is hydrogen or alkyl.

6. A process according to claim 5 wherein R is methyl.
7. A process according to any preceding claim wherein the vinyl monomer is selected from methyl methacrylate, butyl acrylate, butyl methacrylate, acrylonitrile, allyl methacrylate, styrene and mixtures of
5 two or more of said monomers.
8. A process according to any preceding claim wherein the proportion of monomer used as solvent for the isocyanate-terminated polyurethane in step A is from 1.5 to 95% by weight of the total monomers.
10. 9. A process according to claim 8 wherein the proportion of monomer used as solvent is from 2.5 to 80% by weight of the total monomers.
15. 10. A process according to claim 9 wherein the proportion of monomer used as solvent is from 7 to 50% by weight of the total monomers.
11. A coating or film derived from a dispersion prepared by the process as claimed in any of claims 1 to
10.
12. A composite article which includes a film as claimed in claim 11 as an adhesive layer.

20 **Patentansprüche**

1. Verfahren zur Herstellung einer tensidfreien wäßrigen Polymerdispersion, welche ein anionisches wasserdispergierbares Polyurethan und ein Vinylpolymer in einem Gewichtsverhältnis von 10 : 90 bis
25 90 : 10 enthält, bei welchem Verfahren:
 - a) eine Lösung eines anionischen, wasserdispergierbaren, isocyanatabgeschlossenen Polyurethans in mindestens einem Vinylmonomer hergestellt wird,
 - b) die Lösung in einem wäßrigen Medium dispergiert wird,
 - c) das Polyurethan kettenverlängert wird und anschließend entweder
 - 30 d) weiteres Vinylmonomer zugegeben wird und
 - e) die Polymerisation des Vinylmonomers initiiert wird, oder
 - f) die Polymerisation des Vinylmonomers initiiert wird und
 - g) weiteres Vinylmonomer während der Polymerisation zugegeben wird.
- 35 2. Verfahren nach Anspruch 1, bei welchem die hergestellte Dispersion das wasserdispergierbare Polyurethan und das Vinylpolymer in einem Gewichtsverhältnis von 20 : 80 bis 80 : 20 enthält.
3. Verfahren nach Anspruch 1 oder 2, bei welchem das anionische, wasserdispergierbare, isocyanatabgeschlossene Polyurethan ein Reaktionsprodukt ist aus
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 - i) einem organischen Polyisocyanat,
 - ii) einem polymeren Polyol mit einem Molekulargewicht von 500 bis 6000,
 - iii) einer isocyanativen Verbindung mit mindestens einer Säuregruppe und mindestens zwei Gruppen, die gegenüber Isocyanaten reaktiver sind als die Säuregruppe, und gegebenenfalls
 - iv) einem niedermolekularen Polyol mit einem Molekulargewicht unter 500.
- 45 4. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die isocyanativen Verbindung mit mindestens einer Säuregruppe eine Carboxygruppe enthaltendes Diol oder Triol ist.
5. Verfahren nach Anspruch 4, bei welchem das eine Carboxygruppe enthaltende Diol oder Triol eine
50 Dihydroxyalkansäure der Formel



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ist, worin R für Wasserstoff oder Alkyl steht.

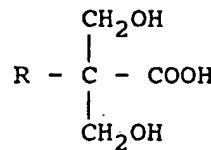
6. Verfahren nach Anspruch 5, bei welchem R für Methyl steht.
- 15 7. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem das Vinylmonomer ausgewählt ist aus Methylmethacrylat, Butylacrylat, Butylmethacrylat, Acrylonitril, Allylmethacrylat, Styrol und Gemischen aus zwei oder mehr dieser Monomere.
- 20 8. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem der Anteil des als Lösungsmittel für das isocyanatabgeschlossene Polyurethan in der Stufe A verwendete Monomer 1,5 bis 95 Gew.% der gesamten Monomere ausmacht.
- 25 9. Verfahren nach Anspruch 8, bei welchem der Anteil des als Lösungsmittel verwendeten Monomers 2,5 bis 80 Gew.% der gesamten Monomere ausmacht.
10. Verfahren nach Anspruch 9, bei welchem der Anteil des als Lösungsmittel verwendeten Monomers 7 bis 50 Gew.% der gesamten Monomere ausmacht.
- 30 11. Belag oder Film, welcher sich von einer durch das Verfahren nach einem der Ansprüche 1 bis 10 hergestellten Dispersion ableitet.
12. Verbundgegenstand, welcher einen Film nach Anspruch 11 als Klebstoffschicht enthält.

Revendications

- 35 1. Procédé de préparation d'une dispersion aqueuse de polymères, dépourvue de surfactant, contenant un polyuréthane anionique dispersable dans l'eau et un polymère vinylique en un rapport pondéral de 10:90 à 90:10, ledit procédé consistant :
 - (A) à former une solution d'un polyuréthane anionique à terminaison isocyanate dispersable dans l'eau dans au moins un monomère vinylique ;
 - (B) à disperser la solution dans un milieu aqueux ;
 - (C) à allonger la chaîne du polyuréthane, puis soit
 - (D) à ajouter une quantité supplémentaire de monomère vinylique, et
 - (E) à déclencher la polymérisation du monomère vinylique, soit
 - (F) à déclencher la polymérisation du monomère vinylique, et
 - (G) à ajouter une quantité supplémentaire de monomère vinylique au cours de la polymérisation.
- 40 2. Procédé suivant la revendication 1, dans lequel la dispersion formée contient le polyuréthane dispersable dans l'eau et le polymère vinylique en un rapport pondéral de 20:80 à 80:20.
- 45 3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel le polyuréthane anionique à terminaison isocyanate dispersable dans l'eau est un produit de réaction :
 - (i) d'un polyisocyanate organique ;
 - (ii) d'un polyol polymérique ayant un poids moléculaire de 500 à 6000 ;
 - (iii) d'un composé réactif avec les isocyanates, comprenant au moins un groupe acide et au moins deux groupes qui sont plus réactifs avec ces isocyanates que le groupe acide et, facultativement
 - (iv) d'un polyol de bas poids moléculaire, ayant un poids moléculaire inférieur à 500.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le composé réactif avec les isocyanates, possédant au moins un groupe acide, est un diol ou triol contenant un groupe carboxy.

5. Procédé suivant la revendication 4, dans lequel le diol ou triol contenant un groupe carboxy est un acide dihydroxyalcanoïque de formule :



dans laquelle R représente l'hydrogène ou un groupe alkyle.

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6. Procédé suivant la revendication 5, dans lequel R représente un groupe méthyle.

7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le monomère vinylique est choisi entre le méthacrylate de méthyle, l'acrylate de butyle, le méthacrylate de butyle, l'acrylonitrile, le méthacrylate d'allyle, le styrène et des mélanges de deux ou plus de deux de ces monomères.

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8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la proportion de monomère utilisé comme solvant pour le polyuréthane à terminaison isocyanate dans l'étape A va de 1,5 à 95% en poids des monomères totaux.

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9. Procédé suivant la revendication 8, dans lequel la proportion de monomère utilisé comme solvant va de 2,5 à 80% en poids des monomères totaux.

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10. Procédé suivant la revendication 9, dans lequel la proportion de monomère utilisé comme solvant va de 7 à 50% en poids des monomères totaux.

11. Revêtement ou film obtenu à partir d'une dispersion préparée par le procédé suivant l'une quelconque des revendications 1 à 10.

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12. Article composite qui comprend un film suivant la revendication 11 comme couche d'adhésif.

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